STYRENE–BUTADIENE COPOLYMERS

Introduction

Styrene–butadiene (SB) copolymers represent one of the largest and most diverse group of polymers in use today. This has come about due to the wide range of properties that can be obtained by modification of styrene–butadiene ratio as well as other material characteristics. Copolymers that contain low levels of styrene, high in butadiene content, show elastomeric behavior, and copolymers that are styrene-rich show thermoplastic behavior. This way SB copolymers can exhibit material performance characteristics ranging from pure elastomeric, as in car tire and other flexible applications, to full thermoplastic, as in injection-molded transparent medical devices. This ability to span such large performance regimes has been a key reason for their widespread use. The other factor that has been critical to the success of SB copolymers has been the commercial availability of the monomers, styrene and butadiene. This article focuses on elastomeric and thermoplastic versions of SB copolymers. In addition to these, SB latex is also used in coatings and paint applications. SB latex is not covered here.

Monomers

Butadiene. Global consumption of butadiene monomer in 1996 was 7.5 million metric tons (1). The largest use of butadiene was for styrene–butadiene rubber, representing 28% of the total volume. Butadiene is manufactured in several different ways. The key industrial processes include recovery of butadiene from ethylene production as a by-product and dehydrogenation using either the
Houdry process or the oxidative dehydrogenation of \( n\)-butenes. Finally in some Asian countries, butadiene is also produced from ethanol.

**Styrene.** Global consumption of styrene monomer in 1998 was 17.9 million metric tons (2). While polystyrene was the largest outlet, SB copolymers (including latexes) consumed a total of 1.95 million metric tons. Styrene monomer is produced by two processes. Ethylbenzene dehydrogenation is the most widespread process used for styrene manufacture, followed by the propylene oxide coproduct route.

**Styrene–Butadiene Rubber (SBR)**

Introduction of automobiles brought with it the need for materials suitable for tire manufacture. In early 1900s, natural rubber was the material of choice. During the World War I restricted access to natural rubber started development programs in Germany. One of the polymers, polydimethylbutadiene, was used for a short while. Further research between two world wars led to the development of Buna S by I.G. Farben (a new company formed by combining Bayer, BASF, and Huls of Germany in 1933). The new rubber incorporated styrene (S stands for Styrol, German name for styrene, in Buna S), improving the performance dramatically. Similarly as U.S. access to natural rubber became restricted during the World War II, a government sponsored research program, known as Government Rubber-Styrene (GR-S), was started. All the rubber producers were organized under the consortium of American Rubber Manufacturers and were overseen by the newly set up Office of Rubber Reserve. The primary product was Buna S.

After the second world war, the United States became aware of the new developments in cold SBR production, which was superior to Buna S type rubbers, and subsequently most of the production facilities in the United States were converted to run the cold SBR process. Cold SBR has become the standard process for emulsion-based SBR production across the globe.

Developments in the anionic polymerization of butadiene were adopted for manufacture of solution SBR. While the emulsion process gave primarily 1,4-cis microstructure in the final product, the solution process gave a lower level of 1,4-cis level, typically around 45%. Furthermore the cis content as well as 1,2-vinyl content could be modified. In addition, better control of branching and molecular weight distribution attainable with anionic process made solution SBR suitable for tire applications, challenging the established use of cold SBR. Developments in the anionic process also led to new copolymer structures in which blocks of polybutadiene can be coupled to blocks of polystyrene, generating a unique class of polymers. Developments in SB block copolymers led to new materials which were thermoplastic in character, unlike SBR which is an elastomer. Solution-process-based thermoplastic SB block copolymers form the basis of the transparent impact polystyrene (TIPS) as well as the other block copolymers used in plastics modification. The block copolymers of styrene and butadiene are the subject of the second part of this article.

**Polymerization Process**

Butadiene and styrene can be copolymerized in a number of ways. Both ionic and free-radical initiations can be used for this purpose. This fact is reflected in
industrial production of SBRs. Initially the free-radical process was entirely based on hot emulsion processes utilizing a polymerization temperature of 50°C. Later developments showed that much improvement can be made to the product if the polymerization temperature can be lowered to around 5°C. As a result the “cold” emulsion process became the process of choice. Today the cold emulsion process accounts for the larger portion of the emulsion SBR market. Introduction of cold emulsion process and advances in anionic polymerization have demonstrated even further advantages, leading to the introduction of the solution process. The solution SBR products make up a smaller part of the consumption but their volume is increasing.

**Cold SBR.** Cold SBR is produced by the emulsion process (3–12). In the emulsion process an emulsion of monomers (styrene and butadiene) is formed in water by the help of an emulsifying agent, usually a soap (13). The monomers in the emulsion are polymerized by a water-soluble initiator fragment, a free radical generated from a hydroperoxide (3) or from an oxidation reduction process. As the free radical enters the emulsion droplet, a micelle, it polymerizes the monomers present.

Emulsion polymerization can be divided into three distinct phases (14) (see Fig. 1). In the nucleation stage, phase I, a free radical is generated (6,15) from the initiating species in the water phase. The most commonly used initiators are the redox systems such as persulfate with ferrous ion (16,17).

$$S_2O_8^{2+} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{2-}.$$  

The free radical then has the possibility to react with monomer dispersed in the system in several states, the most significant of which is micelles (18). Micelles are monomer droplets stabilized by the emulsifying agent. An emulsifying agent contains both oil-soluble and water-soluble parts in its molecular structure, and hence forms the interphase between the water and the dispersed monomeric phase. At the start of phase I, a typical system contains $10^{18}$ micelles/mL and the initiation rate is around $10^{13}$ radicals/(mL·s). As the radicals enter the particles, the polymerization proceeds in the usual manner at a rate $r_p$ with a propagation rate constant $k_p$ and the monomer concentration $[M]$ in the particle (3–5,9).

$$r_p = k_p [M]$$

**Fig. 1.** Three distinct polymerization phases for emulsion polymerization of styrene and butadiene.
As the polymerization continues and monomer is converted to the polymer, the growing micelles continue to absorb more and more emulsifying agent from the medium. As the emulsifier concentration starts to decrease in the reaction medium, there comes a time when the emulsifier concentration falls below a critical micelle concentration. Micelles are formed and maintained only if the emulsifier concentration is above this critical level. The conversion of monomer is typically 15–20% in the first phase.

The growth stage of the process, phase II, starts with micelles becoming polymer particles with a thin layer of surfactant on its surface. At this stage the polymer particles are swollen with monomer that has diffused from the monomer droplets to polymer particles. Major part of the polymerization reaction takes place at the growth stage. The polymerization reaches a steady state inside the swollen polymer particles (10,11). The growth stage ends when most of the monomer is converted to polymer, reaching a conversion level of around 65%. As the monomer concentration drops, the rate of polymerization decreases dramatically as given in Figure 1.

The final stage, phase III, is characterized by complete disappearance of monomer droplets. If the steady state is not maintained by fresh monomer diffusion into the polymer particles, the polymerization rate declines. The unreacted monomer continues to polymerize at a declining rate. If this process is allowed to continue, onset of gelation can take place through chain transfer to polymer.

Rate of polymerization \( R_p \) is given by

\[
R_p = k_p[M][P·]
\]

where \([P·]\) is the concentration of active particles. \([P·]\) is usually expressed as

\[
[P·] = \frac{10^3 N n}{N_A}
\]

where \(N\) is the number of particles (including micelles), \(n\) is the average number of radicals per micelle plus particles, and \(N_A\) is the Avogadro number. Finally, expressing \(R_p\) in its usual units of moles per liter-second gives

\[
R_p = \frac{10^3 N n}{N_A} k_p[M]
\]

The number-average degree of polymerization, \(X_n\), in emulsion polymerization is dependent on the rate \(r_i\) at which primary radicals enter a polymer particle:

\[
r_i = \frac{R_i}{N}
\]

where \(R_i\) is the rate of initiation. In most cases the rate of initiation is same as the rate of termination \(r_t\). This is because as soon as a new radical enters the particle the termination takes place immediately by biradical coupling reaction. Then the
number-average degree of polymerization, \( X_n \), is

\[
X_n = \frac{r_p}{r_i} = \frac{Nk_p[M]}{R_i}
\]

Emulsion polymerization has some unique advantages in comparison to solution or bulk polymerization processes. Most of the advantages are due to the unique polymerization kinetics, such as ability to make high molecular weight monomers at faster polymerization rates. Presence of water enables good temperature control, easy heat removal, and gives lower viscosity.

Selection of components for the emulsion polymerization process is critical. Initiator system, emulsifier, chain transfer agents play a significant role in kinetics of polymerization and in defining the properties of the final product.

A simplified process diagram of cold SBR production facility is given in Figure 2 (19,20). The process can be divided into four units:

1. Feed preparation and clean up
2. Polymerization
3. Coagulation
4. Drying and packaging

Primary function of feed preparation section is to remove impurities from butadiene and styrene monomer. Both monomers contain an inhibitor as

Fig. 2. Process layout showing main components of “cold” emulsion SBR process.
supplied (inhibitors are added to monomers to stop any premature polymerization during transport and storage) and it must be removed by washing with NaOH solution. Following this, water is removed from the monomer stream. Inhibitor and other oxygenated species are removed by passing styrene monomer through an activated alumina column. Other raw materials such as chain transfer agents, usually \(t\)-dodecyl mercaptan (or other mercaptans), hydroperoxide such as \(p\)-methane hydroperoxide, a solution of potassium chloride, sodium dithionate (oxygen scavenger), reducing agent such as sodium formaldehyde sulfoxylate, ferrous sulfate heptahydrate, are prepared in the feed preparation section. Similarly a solution of soaps, usually a mixture of two or more, is also prepared in the feed section.

The polymerization section consists of a series of polymerization reactors jacketed to remove the heat of polymerization. Initially the polymerization reactors are charged with deaerated water and the reactants fed to the reactor. As the polymerization reaction takes place, the heat generated is removed to maintain a reaction temperature of around 5°C, and hence the term “cold” SBR process. Once the desired level of conversion is reached in the displacement reactors, a short stopper is added to terminate the reaction. Then the unreacted monomers are removed by flashing the heated latex. All the unreacted monomers are fed into a recycle tank and returned to the start of the process (13). The latex is then fed to blending tanks to obtain the desired specification and to make the product uniform. Also, at this stage, slightly off-spec material can be blended in.

In the coagulation section, the water is separated from the polymer by chemical means and a slurry of the rubber crumb is obtained. The slurry is then filtered and washed several times. Finally the crumb is further dewatered in an expeller, dried in an expander dryer, and sent to the finishing section.

The finishing section consists of baler, film wrapper, and packaging unit.

**Solution SBR Process.** Solution SBR is based on the anionic process (19,21–25). There are some key differences between emulsion SBR and solution SBR processes, that form the bases for the differences between the two product groups. In the free-radical polymerization process, a polymer chain is initiated by the initiator fragment. In a fraction of a second, several thousand monomers units are added to the growing chain. The polymer chain then terminates through one of three mechanisms: (1) through a coupling reaction with another radical; (2) through disproportionation, where an electron is transferred from one radical to another; or (3) through a chain transfer reaction. Termination leads to a dormant polymer molecule which remains inactive until the end of the polymerization process.

In anionic polymerization, the initiator, typically alkyl lithium, initiates the polymerization process and rapidly reacts with the available monomer molecules. Then the active polymer chains remain active for the duration of the polymerization process. They will continue to polymerize any additional monomer that may be added to the system. The growing polymer chains must be deactivated specifically by the addition of a deactivator at the end of the process.

By far the most common initiator for copolymerization of styrene and butadiene is butyl lithium. Once the polymerization process is initiated, the tendency of the anionic species to add to butadiene or styrene monomer will be different. The polybutadienyl anion prefers to react with another butadiene monomer rather
than a styrene monomer. In fact styrene can be used as a solvent for the anionic polymerization of butadiene if the polymerization reaction is terminated as soon as the butadiene monomer is depleted. If special precautions are not taken, a block copolymer of butadiene and styrene will be obtained. Especially in tire applications, it is very important to have a random copolymer. Special additives must be employed to assure random distribution of styrene units in the copolymer (26).

Solution SBR processes are based on anionic polymerization using butyl lithium initiator. A process flow diagram of the solution SBR process is given in Figure 3, showing major parts of the process. Detailed description of the process has been compiled from the information contained in a series of patents issued to major SBR producers (19,21–25).

The process is made up of three main stages:

1. Feed preparation and clean up
2. Polymerization
3. Finishing

As butyl lithium initiator is very sensitive to water, inhibitor, oxygenated species, and active hydrogen-containing impurities, very stringent feed purification procedures must be carried out. Failure to have high purity will lead to deactivation of the most expensive raw material, butyl lithium [currently around $44/kg (19)]. Trace amounts of water from purified butadiene are removed by passing through a molecular sieve column. Styrene is purified by passing through an alumina column.
The polymerization section consists of a series of continuously stirred tank reactors (24, 25). The solvent (25) (usually cyclohexane) and monomers are fed into the reactor and an initiator as well as a randomizer (usually tetrahydrofuran (THF)) is added. The function of the randomizer is to make sure that no blocks are formed from a single monomer (Hall, Oxolanyl Cyclic Acetals as Anionic PolymerizationModifiers #68). This is because the reactivity ratios of the monomers are not ideal. Usually the reaction temperature is kept less than 110°C to prevent deactivation of the growing chain ends (25). Once polymerization is complete, alcohol is added to terminate the polymerization reaction and the polymer solution is transferred to holding tanks to be blended to increase uniformity. Subsequent steps of washing and filtering remove all the unreacted monomers, THF, and other chemicals.

The finishing section consists of drying, bailing, wrapping, and weighing. The polymer is dried in two steps, then passed through a lump breaker to break any gels, and eventually packaged to the desired specification.

Because of the significant difference in polymerization characteristics, emulsion and solution processes produce SBR with a different balance of properties. These differences are a result of the molecular structure, branching, molecular weight distribution, and microstructure. In general, the solution SBR process provides a higher capability to modify the molecular parameters.

Some of the key advantages of solution SBR over emulsion SBR are molecular weight and molecular weight distribution control, low levels of branching, lower levels of contaminants, and higher degree of control over molecular topology. These characteristics provide improved performance to end-use applications as in tire manufacture. Solution SBR can lead to better balance between treadwear, traction, and rolling resistance. These three are the key properties that a tire manufacturer will aim to optimize (26).

The solution SBR process can control the molecular weight distribution and branching very effectively. During emulsion process the polymer chains grow in a very short while and then terminate, whereas in the solution process the growing chains are active until the monomers are consumed or a terminating agent is added. As a result the chains produced in solution process tend to be uniform in length whereas emulsion process leads to a broad distribution as chains that grow at different times in the process tend to have different molecular weight. The branching is a random process in the emulsion SBR route whereas it must be specifically incorporated by introducing branching agents during the solution process.

The monomeric unit in polybutadiene can exist in three distinct forms: 1,4-cis, 1,4-trans, and 1,2-vinyl (see Fig. 4). The relative portions of each one of these

![Fig. 4. Different types of microstructure for polybutadiene.](image-url)
microstructures have a strong influence on the final properties of the polymer. Both the solution SBR and emulsion SBR processes give similar levels of 1,4 structures. Emulsion process gives a 1,2-vinyl level of about 20%. Depending on the specifics of the process, the solution process can give anywhere from about 8 to 60%.

**Processing of SBR**

SBR as manufactured, is an elastomeric material that requires further processing to convert it to a final article for end use. The processing accomplishes three key objectives. First of all it gives the article its final shape, then it incorporates additives that are required by the targeted end use, and finally causes cross-linking of the rubber. Without cross-linking, the rubber will not be usable, as it is a soft “gummy” material that would not retain its shape during use.

Typical processing of SBR is done in two stages (27). In the first stage, non-reactive components are mixed with the rubber to obtain a good dispersion. At this stage, to prevent any cross-linking, the cross-linking agents and accelerators are not added. The first-stage processing is called nonproductive stage as no cross-linking occurs at this stage. SBR (and optionally, a second rubber) is mixed with additives such as fillers, oils, antioxidants, stabilizers, and antiozonants, as well other specific additives. Fillers are added to “extend” the rubber. By far the most common filler is carbon black. Their function is usually to reduce the cost of the overall formulation and also to improve physical properties such as tensile strength. The carbon black fillers come in standard forms (28). A list of most common fillers and their function is given in Table 1. A large number of other components are used in the manufacture of SBR articles.

Oil extenders include naphthenic, aromatic, and paraffinic oils. Their function is to soften the rubber for processing. Other processing oils include castor and tall oils as well as low molecular weight resins.

Once the nonproductive stock is mixed in an internal mixer in the second-stage cross-linking agents, accelerators are added to the nonproductive stock, which can then be shaped into final form and cured. The curing process is a chemical cross-linking reaction that builds bonds between rubber molecules.

SBR contains active double bonds on the polymer backbone. Cross-linking reactions are carried out by generating free radicals which react to form content bonds. Without the help of acceleration this reaction requires long times and high temperatures. By proper choice of activators and accelerators both the curing temperature and curing speed can be tailored for a given application.

By far the largest volume of SBR goes into automobile tires, representing some 80% of the total volume (30). In addition to tires, many other applications from gaskets to hoses also use SBRs. The single most important property of SBRs is their glass-transition temperature \( T_g \). For tire applications \( T_g \) must be in a certain range, typically \(-70 \) to \(-50 \)°C. Proper choice of \( T_g \) is important for control of friction and traction. If the \( T_g \) is too high, the rubber can loose its rubbery properties at low temperatures. On the other hand, too low a \( T_g \) can also cause problems. At very low \( T_g \)'s, the traction at wet roads and moderate temperatures can suffer. In general, lower the \( T_g \), better the treadwear. Tire manufacturers must
Table 1. Different Classes of Materials Used in SBR Processing and Their Function

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fillers</td>
<td>Carbon black</td>
<td>Reinforcing filler improves physical properties and reduces cost</td>
</tr>
<tr>
<td></td>
<td>Calcium carbonate</td>
<td>Reduces cost and increases tensile strength. Both reinforcing (small</td>
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<tr>
<td></td>
<td></td>
<td>particle) and nonreinforcing (coarse (29)) types exist</td>
</tr>
<tr>
<td></td>
<td>Clay</td>
<td>Reduces cost and increases tensile strength</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>Improves physical properties</td>
</tr>
<tr>
<td>Processing aids</td>
<td>Naphthenic/aromatic/</td>
<td>Extender (for softening of rubber)</td>
</tr>
<tr>
<td></td>
<td>paraffinic oil</td>
<td></td>
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<tr>
<td></td>
<td>Castor/tall oil</td>
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<tr>
<td>Vulcanization</td>
<td>Sulfur</td>
<td>Cross-linking</td>
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<tr>
<td>agents</td>
<td>Disulfide organic</td>
<td>Fast accelerator, low temperature curing</td>
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<td></td>
<td>hydroperoxides</td>
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<tr>
<td></td>
<td>Tetramethylthiuram</td>
<td>Low sulfur cross-linking</td>
</tr>
<tr>
<td>Accelerators</td>
<td>Mercaptobenzothiazole</td>
<td>Fast accelerator, low temperature curing</td>
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<tr>
<td></td>
<td>dithiocarbomates</td>
<td></td>
</tr>
<tr>
<td>Accelerators and</td>
<td>Zinc oxide, stearic acid</td>
<td>Cross-linking</td>
</tr>
<tr>
<td>activators</td>
<td>diethanolamine</td>
<td></td>
</tr>
<tr>
<td>Antioxidants</td>
<td>Phenolics</td>
<td>Nonstaining stabilizers</td>
</tr>
<tr>
<td></td>
<td>Phosphites</td>
<td>Good stabilizers for SBR</td>
</tr>
<tr>
<td>Antiozonants</td>
<td>Diaryl-phenylene diamine</td>
<td>Low cost antiozonant</td>
</tr>
</tbody>
</table>

balance many compiling requirements of traction, wear, and rolling resistance by proper selection of $T_g$ for this application. $T_g$ has a strong influence on the hysteresis imparting rolling resistance and fuel consumption.

Two key variables that influence glass-transition temperature are styrene content and percentage of 1,2-vinyl in the microstructure. For emulsion process, the relationship between $T_g$ and styrene content is as follows (31):

$$T_g = -78 + \frac{128S}{1.0 - 0.5S}$$

where $S$ is the weight fraction of styrene in the copolymer.

Similarly for 1,2-vinyl content, the following relationship holds:

$$T_g = \left[1/(0.00578 - 0.0031S - 0.00212V + 0.00212VS)\right] + 273$$

where $V$ is the weight fraction of 1,2-vinyl units in the butadiene portion of the copolymer. These equations are valid only for emulsion SBRs. In the case of solution SBR, some of the styrene units are present as short block and are not truly random copolymers.
Specifications, Testing, and Environmental Aspects

SBRs are characterized at different stages of their manufacture and use, utilizing several types of test procedures. During the manufacturing stage of the rubber, a series of tests are carried out to establish solids content (conversion), molecular weight, and chemical composition. Conversion is measured by just removing solvent and unreacted monomers, while chemical composition can be measured by either IR spectroscopy or by titration. The molecular weight and molecular weight distribution are determined by gel permeation chromatography.

Once the polymers are manufactured further characterization takes place prior to processing or during the process itself. The two key properties that are critical are \( T_g \) and Mooney viscosity. The most convenient way to measure the \( T_g \) is by differential scanning calorimeter. Mooney viscosity is an industry specific test procedure that is used for assessing the processability of the rubber. Mooney viscosity (ASTM D1646) is measured by rotation of a disk inside a cavity under pressure. This equipment does not measure the viscosity, but rather the torque required to rotate the disk at 100°C at a rate of 2 rpm. The results are usually given as

\[
50 - \text{ML} 1 + 4(100^\circ C)
\]

where 50-ML is the viscosity number, L indicates the larger of two rotor diameters used (other one being a smaller one for higher viscosity rubbers), 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken, and 100°C indicates the temperature of the test.

In recent years dynamic mechanical testing has become an important means in correlating the performance of tires to molecular structure. Especially \( \tan \delta \) (ratio of elastic modulus to viscous modulus) has been used for understanding rolling resistance, skid resistance, and wear (26).

During the manufacturing process, primary health and environmental concerns relate to emissions and exposure. In most countries there are strict regulations concerning exposure to styrene and butadiene monomers. In the United States the exposure limits for styrene monomer is set at a time weighted average of 50 ppm. The same value for butadiene is 10 ppm. During the processing, the breakdown of additives is a major concern. Use of secondary amines are regulated in some countries through monitoring of volatile nitrosamine generation. One of the primary environmental concerns for the rubber industry is the growing mountains of used tires. No significant outlet has been found for the recycling of the rubber in tires.

Styrene–Butadiene Block Copolymers

Emulsion and solution SBRs are made up of butadiene and styrene units that are randomly distributed along the polymer backbone. In the case of free-radical-polymerization-based emulsion process, the radical center randomly polymerizes both the styrene and butadiene units. The frequency by which these monomers
are incorporated into the growing polymer chain is determined by the reactivity ratios and the concentration of the monomers. In free-radical polymerizations the growing polymer chains have very short life spans in the order of less than a second. This eliminates any possibility of using sequential monomer addition techniques to make block copolymers. The only way to make block copolymers in the free-radical process is through incorporation of active sites into the polymer backbone which at a later stage is activated by heat or radiation in the presence of another monomer as indicated below.

This route has been used extensively to make several types of block copolymers that cannot be made by anionic polymerization techniques. Systems where \( R \) is a peroxide group (32,33), diazo groups (34), hydroperoxide groups (35), or living free-radical groups (29,35) are used. Even though this route to block copolymers has been extensively investigated academically, no significant industrial application has been developed. Recent advances in living free-radical polymerizations indicate that this route might be more suitable for industrial use.

Industrially the most significant route to block copolymerization of styrene and butadiene is through anionic polymerization. The living nature of the anionic polymerization makes it possible to produce block copolymers of styrene and butadiene mostly through sequential addition of monomers.

Properties of Block Copolymers. Random copolymers of styrene and butadiene form homogeneous, one-phase systems showing typical characteristics of a single-phase polymer, such as a single \( T_g \). In contrast the block copolymers of styrene and butadiene are two phase systems, with distinct domains of polybutadiene and polystyrene. As long as polystyrene domains are over 6000 amu in molecular weight, a two-phase system develops (36). The actual morphology of the block copolymer depends on the weight ratio of styrene and butadiene in the copolymer (Fig. 5). At low levels of styrene, a continuous polybutadiene phase develops with small spherical structures of polystyrene dispersed in the system (Fig. 6). As the styrene content of the block copolymer increases, spherical inclusions of polystyrene become elongated into cylindrical structures, becoming platelets at higher styrene levels (15–45%). At about 45% styrene level, co-continuous structures develop with alternating layers of polystyrene and polybutadiene.

The nature of SB block copolymers is defined by the weight ratio of styrene and butadiene. Those that contain more than 50 wt% butadiene are elastomers showing distinct elastomeric behavior. Industrially most polymers of this type contain 10–40 wt% styrene. As the styrene content increases the elastomeric nature of the block copolymer decreases. If the styrene content is above 50 wt% then a thermoplastic resin is obtained. These materials have the typical properties of
Fig. 5. Dependence of copolymer morphology on copolymer ratio in block copolymers of styrene.

Fig. 6. A graphical representation of SB block copolymer structure at ambient temperature, with styrene content of 15% or less. Polystyrene phase (dark short lines) is presented as spherical domains dispersed in polybutadiene phase.

thermoplastic resins. As the styrene content approaches 100%, the resins become similar to high impact polystyrene (HIPS).

Manufacturing Process for Block Copolymers. Manufacturing of block copolymers is similar to solution SBR process, as they both use anionic polymerization. For elastomeric block copolymers the process is similar to solution SBR process. This is because the same feed purification and reactor layout is needed for producing elastomeric SBR polymers. The main difference between the solution SBR process and block copolymer production process is due to the fact that the styrene monomer distribution in the solution process is random while in block copolymers styrene is present as blocks (sequences of styrene monomer forming a polystyrene segment). In the process styrene and butadiene monomers are charged to the reactors at the same time. In the block copolymer process, first the butadiene segment is polymerized in the absence of styrene monomer. As the conversion of butadiene monomer nears completion, styrene monomer is added. Depending on the actual sequence, the transition from butadiene to styrene
segment can be graded, whereby the concentration of monomer units in the backbone changes from pure butadiene to a mixture of styrene and butadiene, eventually becoming pure styrene. These types of copolymers are referred to as tapered block copolymers. A short transition from butadiene to styrene units can also be achieved by making sure that all the butadiene is reacted prior to addition of styrene. In the case of triblock copolymers (SBS), two techniques are employed for manufacture. In the first case a sequential addition of monomers is used. First, styrene is polymerized until completion, followed by addition of butadiene and polymerization to completion. At the final stage, additional styrene monomer is added to form the triblock structure (Fig. 7). The second method is based on the use of bifunctional anionic initiators (37,38). With this type of initiator, the butadiene segment is produced first, followed by addition of styrene. As the bifunctional initiator grows the polymer from both ends, a triblock copolymer is obtained with two monomer addition steps versus the tri monomer addition steps of the monofunctional initiator case. Alternatively a coupling agent can also be used to produce SBS block copolymers with two steps of monomer addition (39,40). Elastomeric block copolymers can be finished in a manner similar to solution SBR if styrene content is relatively low. At above 25–30% styrene content the block copolymer loses its rubbery nature and becomes a relatively tough, difficult to bale product. At around 40% styrene content the product is powdery and cannot be baled easily. In the case of elastomeric block copolymers, unreacted monomers and solvent can be removed by steam stripping (41).

In the literature, many routes to synthesis of block copolymers are given, but on commercial scale, only the anionic solution process is used. In the case of solution SBR great care is taken to assure random distribution of monomeric units. In block copolymers great care is taken to assure that the butadiene and styrene units exist as blocks. The thermoplastic block copolymers, especially those with

![Fig. 7. Synthesis of triblock copolymers (S–B–S) with sequential monomer addition.](chart)
styrene contents above 65 wt%, can be finished with conventional thermoplastic finishing equipment.

The feed preparation and reactor sections of thermoplastic block copolymer production process are similar to the solution SBR process (36,39,40,42–45). Styrene, butadiene, and solvent are purified by distillation, followed by passing the reactants and solvent over alumina columns and molecular sieves (Fig. 8).

**Thermoplastic Block Copolymers.** Most well-known thermoplastic block copolymers are the K-Resin family (36,46) (Phillips Petroleum Co.). These contain about 27% butadiene in a star-block form (Fig. 9).

![Fig. 8. Process layout showing main components of solution SB block copolymer manufacturing process.](image)

![Fig. 9. Synthesis of star-block copolymers.](image)
K-Resin is made up of a star-block copolymer where the inner polybutadiene segments are of about the same molecular weight while the outer polystyrene segments are of different molecular weight (47). This enables accurate control of polybutadiene segment thickness, ensuring improved clarity. To achieve optimum clarity, the polybutadiene segment thickness must be about one-tenth of the wavelength of visible spectrum or less (see Elastomers, Thermoplastic).

**Processing of Block Copolymers.** Elastomeric block copolymers contain blocks of styrene units that form hard segments below the glass-transition temperature of polystyrene. In most uses they do not need to be cured as the hard polystyrene segments act as cross-linking units below the glass-transition temperature of polystyrene (48,49). The block copolymers are seldom used in their pure form for fabrication of end-use articles. Most of the time they will be blended with other rubbers. By far the largest use of these types of block copolymers is for impact modification of polystyrene where they are blended with a polystyrene resin in a compounding or an extruder. They are also used in the manufacture of special grades of HIPS, mostly high gloss types, for injection molding or as a gloss layer for the co-extrusion of HIPS. One of the critical issues for thermoplastic SB block copolymer processing is cross-linking of the rubber phase. Special care must be taken to ensure processing temperatures do not exceed 240°C (51). If higher temperatures are needed, then the residence time must be minimized. Formation of cross-linked rubber is particularly important for the extrusion thermoforming process as these processes generate large amounts of recycle which is then blended with the virgin resin. In this way certain portions of the resin can end up going through the processes several times, further increasing the chances of gel formation. Presence of gel is detrimental to thermoformed articles as they cause significant problems in the appearance and wall thickness distribution for the thermoformed articles.

**Economic Aspects and Use**

Block copolymers of styrene and butadiene are extensively used in blends as well as neat products. Most of the blends are made with polystyrene resins, where addition of block copolymer improves the toughness of otherwise brittle polystyrene. Such materials find widespread use in food packaging, from yogurt cups to polystyrene film used for food packaging. Some volume of copolymer is also used as an impact modifier in the manufacture of specialty grades HIPS.

Block copolymers containing 20–40% styrene are also useful as impact modifiers for ignition-resistant HIPS as well as other polystyrene resins. Kraton® rubbers are available from Shell Chemical Co. and Vector® rubbers are available from Dexco Polymers (a joint venture between The Dow Chemical Co. and The Exxon Chemical Co.). Both grades are used extensively for this purpose as are other similar products from other suppliers. Kraton rubbers are usually triblock copolymers of SBS type. The center block is polybutadiene with terminal blocks of polystyrene (49–51). By far the largest use of block copolymers is in the form of TIPS resins. There are a number of suppliers, with Phillips Petroleum and BASF
Table 2. Properties of K-Resin Grades KR01 and KR03 from Philips Petroleum Co.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM test method</th>
<th>KR01</th>
<th>KR03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>D1505</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>Melt flow rate, g/10 min</td>
<td>D1238</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Tensile yield strength 50 mm/min, MPa</td>
<td>D638</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>Elongation to break, %</td>
<td>D638</td>
<td>20</td>
<td>160</td>
</tr>
<tr>
<td>Flexural yield strength, MPa</td>
<td>D790</td>
<td>44</td>
<td>34</td>
</tr>
<tr>
<td>Flexural modulus, MPa</td>
<td>D790</td>
<td>1492</td>
<td>1414</td>
</tr>
<tr>
<td>Heat deflection temperature 1.8-MPa fiber stress, °C</td>
<td>D638</td>
<td>77</td>
<td>73</td>
</tr>
<tr>
<td>Izod impact strength 3.2-mm specimen, notched, J/m</td>
<td>D252</td>
<td>22</td>
<td>41</td>
</tr>
<tr>
<td>Hardness, Shore D</td>
<td>D2740</td>
<td>75</td>
<td>65</td>
</tr>
<tr>
<td>Vicat softening point, °C</td>
<td>D1525</td>
<td>93</td>
<td>87</td>
</tr>
<tr>
<td>Light transmission, %</td>
<td></td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

*a*To convert MPa to psi, multiply by 145.

*b*To convert J/m to ft-lbf/in., divide by 53.38.

being the largest producers. Phillips Petroleum product is supplied under the trade name K-Resin, with several grades for extrusion and injection molding (51). BASF also supplies a number of grades under the trade name Styrolux. Clarity, toughness, and rigidity are the key combinations for TIPS, making the product very desirable for both extrusion-thermoforming and injection-molding applications. In most cases the TIPS resins are blended with polystyrene depending on the toughness requirements of the final formulation. Properties of two grades of K-Resin are given in Table 2 (51) (see ELASTOMERS, THERMOPLASTIC).

Most significant environmental issues with respect to block copolymer synthesis relate to manufacturing process, taste and odor issues in end use, and solid waste in final disposal of these polymers. Manufacturing process issues relate to industrial hygiene, exposure, and volatile organic emissions. In end use, block copolymer/polystyrene blends tend to have taste and odor issues, especially for sensitive food packaging applications.

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